

# THE VAPOR PRESSURE OF ICE AND OF WATER BELOW THE FREEZING POINT

551.57 : 551.578.4

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[National Research Council, Washington, Aug. 20, 1924]

## INTRODUCTION

This communication embodies the results of a critical examination of the available vapor pressure data on ice and supercooled water, and was undertaken for the purpose of computing tables of vapor pressures for inclusion in International Critical Tables. At the request of the editor of the REVIEW, the author has added some footnotes in further explanation of some of the thermodynamic principles used.

## THE VAPOR PRESSURE OF ICE

In preparing a table of vapor pressures of ice the older investigations on this subject can not be taken into account, owing, if for no other reason, to lack of definition of the temperature scales employed by the investigators. In computing the table given below, I have therefore based the calculations on the concordant measurements by (1) Weber (in the physical laboratory of the University of Leyden) and (2) Scheel and Heuse (at the Reichsanstalt). These investigations cover the range  $-100^{\circ}$  to  $0^{\circ}$  C.

The interpolation equation for this temperature range was obtained by integrating the Clausius-Clapeyron equation<sup>1</sup>

$$\frac{dp}{dT} = \frac{L_s}{(v - V)T} \quad (1)$$

using the best available thermal data, as set forth below. In integrating the equation the perfect gas law was assumed for the vapor and the term  $Vdp$ , involving the volume,  $V$ , of the solid, was at first included in the integration. It was found, however, that the terms to which it gave rise in the integral were negligible. The integral was finally obtained in the following form:

$$\log_{10} p = \frac{A}{T} + B \log_{10} T + CT + DT^2 + I \quad (2)$$

where  $T$  is the absolute centigrade temperature and  $A$ ,  $B$ ,  $C$ ,  $D$ , and  $I$  are constants.

The constant  $A$  was based upon the latent heat of vaporization of ice at  $0^{\circ}$  C., which was computed from Dieterici's value for the latent heat of vaporization of water at  $0^{\circ}$  (i. e., 2493 Int. Joules per gram) and Dickinson and Osborne's value<sup>2</sup> for the latent heat of fusion of ice at  $0^{\circ}$  (i. e.,  $79.76 \pm 0.02$  cal.<sub>20</sub> per gram).

The constant  $B$  was based upon the value 0.5057 cal.<sub>20</sub>, the heat capacity of ice<sup>3</sup> per gram at  $0^{\circ}$  C. and the value 0.457 cal.<sub>20</sub> the heat capacity of water vapor<sup>4</sup> per gram at  $0^{\circ}$  C.

The integration constant,  $I$ , was evaluated by taking the well-established value  $p = 4.579$  mm. at  $0^{\circ}$ , and the constants  $C$  and  $D$  were evaluated from two experimental values for  $p$ , one in the neighborhood of  $-100^{\circ}$  based upon Weber's measurements and the other in the neigh-

borhood of  $-50^{\circ}$  based upon concordant measurements by Weber and by Scheel and Heuse.

The equation thus obtained is

$$\log_{10} p = \frac{-2445.5646}{T} + 8.2312 \log_{10} T - 0.01677006 T + 1.20514 \times 10^{-5} T^2 - 6.757169 \quad (3)$$

Using this equation to obtain  $p_{\text{calc}}$ , a deviation graph,  $p_{\text{calc}} - p_{\text{obs}}$ , was then prepared and is displayed in Figure 1. An examination of this graph shows that the equation satisfactorily expresses the experimental data throughout the region from  $-100^{\circ}$  to  $-20^{\circ}$ . Between  $-20^{\circ}$  and  $0^{\circ}$  the only extensive experimental data available are those of Scheel and Heuse, which deviate rather widely from the calculated values for this region. In a later paper<sup>5</sup> by the same authors, attention is called to the fact that

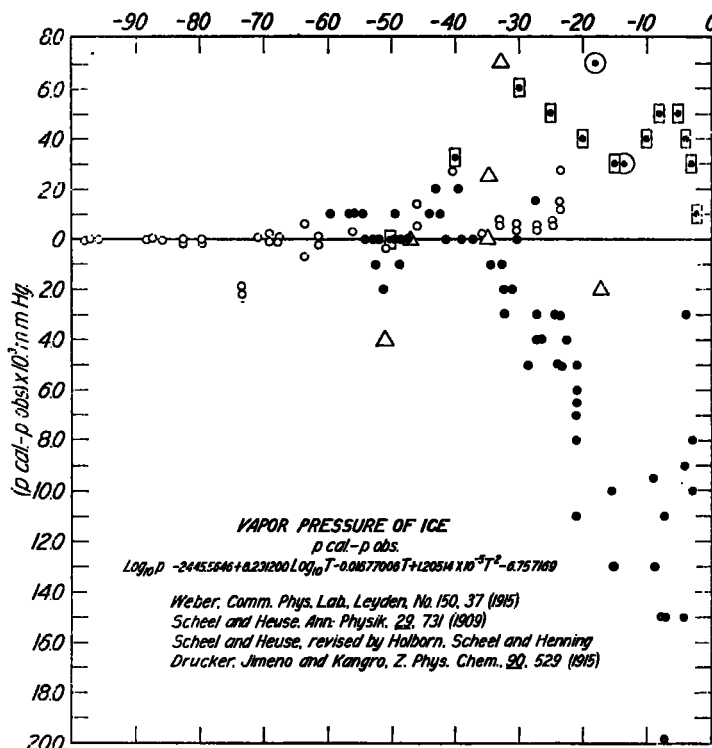


FIG. 1

our knowledge of the relation between the platinum scale (platinum-resistance thermometer) and the gas-thermometer scale in this interval is still in a very unsatisfactory state and that consequently the measurements in this region require revision. Some such revision appears to have been made by the Reichsanstalt, for, in the recent book by Holborn, Scheel, and Henning<sup>6</sup> quite different values are given for the vapor pressure of ice between  $-50^{\circ}$  and  $0^{\circ}$ . The nature of the revision made by them is not indicated, but, judging from the discussion referred to above, the revision is perhaps based upon a modification of the Callender interpolation equation for the platinum-resistance thermometer. Their revised values are also plotted in Figure 1. While the revised values agree somewhat better with equation (3), the differences are now in the opposite direction and are still much larger than can be accounted for by any obvious source of error in the pressure measurements.

<sup>1</sup>  $p$ —vapor pressure;  $T$ —absolute temperature;  $L_s$ —latent heat of sublimation per gram-mole;  $v$ ,  $V$ —orthobaric volumes per gram-mole for the vapor and liquid, respectively. For a simple derivation of this equation, see Washburn's "Principles of Physical Chemistry," p. 482.

<sup>2</sup> Dickinson and Osborne, *Bull. Bur. Stands.* 12, 76 (1915).

<sup>3</sup> Dickinson and Osborne, loc. cit.

<sup>4</sup> Estimated.

<sup>5</sup> Scheel and Heuse, *Ann. Physik*, 31, 733 (1910).

<sup>6</sup> "Wärmepressuren der Physikalisch-Technischen Reichsanstalt," Braunschweig, 1919.

It seems, therefore, necessary to reject the experimental data in this region on account of the uncertainty in the temperature measurements and to assume that the calculated values are the correct ones. This is the more justifiable since the equation has a sound thermodynamic basis and the constants  $C$  and  $D$ , which are the only ones determined empirically, have practically no influence upon the calculation in this region; that is, the omission of the terms containing  $C$  and  $D$  and a re-evaluation of  $I$  for this range gives an equation yielding substantially the same values of  $p$ .

#### THE VAPOR PRESSURE OF LIQUID WATER BELOW THE FREEZING POINT

Having established the vapor pressure table for ice, the most reliable method of arriving at the values for the vapor pressure of undercooled water is through the thermodynamic relation which connects the two sets of vapor pressures. This relation, which is a direct consequence of the Second Law of Thermodynamics,<sup>7</sup> is:

$$d \log_e \frac{p_w}{p_i} = d \log_e r = \frac{-L_F dT}{RT^2} \quad (4)$$

where  $p_w$  and  $p_i$  are the respective vapor pressures of water and of ice at the absolute temperature  $T$ ,  $L_F$  is the latent heat of fusion per mole of ice at  $T^\circ$  and  $R$  is the gas constant. In order to integrate this equation, we must first express  $L_F$  as a function of the temperature. The Law of Conservation of Energy gives us the following function:

$$L_F = L_{F0} + at + 1/2 bt^2 + 1/3 ct^3 \quad (5)$$

where  $t$  is the centigrade temperature, and  $a$ ,  $b$ , and  $c$  are constants which can be obtained and numerically evaluated from the following empirical relations:

$$s_w = 1.0092 - 0.001080 t + 0.000036 t^2 \quad (6)$$

where  $s_w$  is the heat capacity of liquid water in cal.<sub>15</sub> per gram:<sup>8</sup>

$$s_i = 0.5952 + 0.001861 t \quad (7)$$

where  $s_i$  is the heat capacity of ice<sup>9</sup> in the same units:

$$\Delta s = 18.015 (s_w - s_i) = a + bt + ct^2 \quad (8)$$

$$= 9.079 - 0.05300t + 0.00065t^2 \quad (9)$$

and

$$L_{F0} = 1435.5,^{10} \text{ cal.}_{15} \text{ mole}^{-1} \quad (10)$$

<sup>7</sup> The Second Law of Thermodynamics is the mathematical formulation of the principle that the autogenous flow of heat is always from a higher to a lower temperature, never in the reverse direction. This law, applied to the vaporization of a solid or a liquid having a low vapor pressure, yields the relation (Washburn, loc. cit.):

$$d \log_e p = \frac{L dT}{RT^2}$$

where  $p$  is the vapor pressure;  $L$ , the latent heat of vaporization per mole (both at  $T^\circ$  absolute); and  $R$  is the gas constant. Thus, for ice and water, respectively, this equation becomes

$$d \log_e p_i = \frac{L_i dT}{RT^2}$$

and

$$d \log_e p_w = \frac{L_w dT}{RT^2}$$

Subtracting the first equation from the second gives us equation (4), since, according to the law of the conservation of energy,

$$L_w - L_i = L_F$$

The conservation law also gives us the relation

$$\frac{dL_F}{dT} = s_w - s_i$$

the integral of which is our equation (5). (Vide Washburn loc. cit., p. 307.)

<sup>8</sup> Numerical coefficients deduced from the data of Barnes and Cooke [Phys. Rev. 16, 65 (1903)] at  $5^\circ$ ,  $0^\circ$ , and  $-5^\circ$  C.

<sup>9</sup> Equation obtained by Dickinson and Osborne, loc. cit., valid between  $-40^\circ$  and  $0^\circ$  C.

<sup>10</sup> From the determination by Dickinson and Osborne, loc. cit.

Combining equation (5) with (4), integrating, expanding the logarithm term in powers of  $t$ , and performing the divisions indicated so as to obtain all terms except the first in powers of  $t$ , yields finally the relation,

$$R \log_e r = \frac{-L_{F0}t}{T_0(T_0+t)} - \frac{1/2a}{T_0^2} t^2 + \left[ \frac{3/4a}{T_0^3} - \frac{1/2b}{T_0^2} \right] t^3 - \left[ \frac{3/4a}{T_0^4} - \frac{1/4b}{T_0^3} + \frac{1/2c}{T_0^2} \right] t^4 \quad (11)$$

Putting  $R = 1.9869 \text{ cal.}_{15} \text{ deg.}^{-1} \text{ mole}^{-1}$ ,  $T_0 = 273.1^\circ \text{C}$ , and evaluating  $a$ ,  $b$ , and  $c$ , as indicated above, gives finally

$$\log_{10} p_w = \frac{-1.1489t}{(273.1+t)} - 1.330 \times 10^{-6} t^2 + 9.084 \times 10^{-8} t^3 - 1.08 \times 10^{-9} t^4 + \log_{10} p_i \quad (12)$$

It will be noticed that no vapor pressure data are required in deriving this equation.

For an accuracy of 0.001 mm. Hg, in the value of  $p_w$ , the  $t^4$  term is negligible down to  $-40^\circ$ , the  $t^3$  term down to  $-11^\circ$ , and the  $t^2$  term down to  $-2^\circ$ . All of the numerical constants in the equation are known to two more significant figures than are required for an accuracy of 0.001 mm. of Hg in  $p_w$ .

When we compare the values of  $p_i - p_w$  calculated by means of equations (12) and (3) with the corresponding differences between the directly measured values obtained by the Reichsanstalt, we find that the maximum value of  $(p_i - p_w) \text{ calc.} - (p_i - p_w) \text{ obs.}$  is only 0.004 mm. at  $-16^\circ$  and decreases as  $0^\circ$  is approached. In other words, the pressure measurements of the Reichsanstalt are consistent, although, as explained above, the corresponding temperatures are uncertain, an uncertainty in the temperature scale having a much smaller influence on  $p_w - p_i$  than it does on  $p_w$  and  $p_i$  separately.

#### THE VAPOR PRESSURE OF ICE UNDER ATMOSPHERIC PRESSURE

The measured values of the vapor pressure of ice and the table given below, which is based upon these values, are for ice under its own vapor pressure. In contact with the atmosphere, ice has a slightly higher vapor pressure than when in contact only with its own vapor. In order, therefore, to obtain the vapor pressure of ice under atmospheric conditions, it is necessary to add a small correction to the values given in Table 1 below.

This correction expressed in per cent,  $100 \frac{\Delta p}{p}$ , is given by the equation

$$100 \frac{\Delta p}{p} = \frac{100V}{RT} (B - p) \quad (13)$$

where  $V$  is the molal volume of ice at  $T^\circ$  abs. and  $B$  is the barometric pressure.  $V$  is in general a function of  $T$ , but by employing an average value the above equation may, for all practical purposes, be written

$$100 \frac{\Delta p}{p} = \frac{20}{T} \quad (14)$$

Thus, for example, to find the vapor pressure of ice at  $-5^\circ \text{C}$ , under atmospheric pressure,

$$100 \frac{\Delta p}{p} = \frac{20}{268} = 0.075\%$$

From Table I we find  $p=3.013$  at  $-5^{\circ}$ , which, increased by 0.075%, gives 3.015, the vapor pressure of ice in contact with the atmosphere at  $-5^{\circ}$  C.

#### THE VAPOR PRESSURE OF WATER IN EQUILIBRIUM WITH THE ATMOSPHERE

Just as in the case of ice, the vapor pressure of water in contact with the atmosphere differs from its vapor pressure when in contact with its own vapor only. For water below  $0^{\circ}$  C. the correction may, for all practical purposes, be computed from equation (14). For higher temperatures, the following more exact equations may be employed:

$$100 \frac{\Delta p}{p} = 0.0775 - 3.13 \times 10^{-4} t \quad (\text{valid up to } t = 40^{\circ} \text{ C.}) \quad (15)$$

and

$$100 \frac{\Delta p}{p} = 0.0652 - 8.75 \times 10^{-5} p \quad (\text{valid above } 50^{\circ} \text{ C.}) \quad (16)$$

In these equations both the effect of the external pressure, as such, and the effect of dissolved air are taken into account. At high temperatures ( $70^{\circ}$ – $80^{\circ}$  C.) this correction amounts to more than 0.1 mm.

TABLE 1.—The vapor pressure of ice

Computed from the equation

$$\log_{10} p = \frac{-2445.5646}{T} + 8.2312 \log_{10} T - 0.01677006 T + 1.20514 \times 10^{-4} T^2 - 6.757169 T \text{ mm. Hg.}$$

Based upon the measurements of Weber (Comm. Phys. Lab. Leyden No. 150, 37 1915) and Scheel and Heuse (Ann. Physik 29, 731 [1909]).

$$T = 273.1 + t$$

$-90^{\circ}$  to  $-30^{\circ}$ . unit, 0.001 mm. Hg

t	0	1	2	3	4	5	6	7	8	9
$^{\circ} \text{C.}$										
-90	0.070	0.056	0.043	0.033	0.025	0.018	0.012	0.008	0.005	0.003
-80	0.40	0.34	0.29	0.24	0.20	0.17	0.14	0.12	0.10	0.08
-70	1.94	1.67	1.43	1.23	1.05	0.90	0.77	0.66	0.56	0.47
-60	8.06	7.03	6.14	5.34	4.64	4.03	3.49	3.03	2.61	2.23
-50	29.5	26.1	23.0	20.3	17.8	15.7	13.8	12.1	10.6	9.25
-40	96.6	86.2	76.8	68.4	60.9	54.1	48.1	42.6	37.8	33.4
-30	285.9	257.5	231.8	208.4	187.3	168.1	150.7	135.1	120.9	108.1

$-30^{\circ}$  to  $0^{\circ}$ . mm. Hg

t	0.0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
$^{\circ} \text{C.}$										
-29	0.317	0.314	0.311	0.307	0.304	0.301	0.298	0.295	0.292	0.289
-28	0.351	0.348	0.344	0.341	0.337	0.334	0.330	0.327	0.324	0.320
-27	0.389	0.385	0.381	0.377	0.374	0.370	0.366	0.363	0.359	0.355
-26	0.430	0.426	0.422	0.418	0.414	0.409	0.405	0.401	0.397	0.393
-25	0.476	0.471	0.467	0.462	0.457	0.453	0.448	0.444	0.439	0.435
-24	0.526	0.520	0.515	0.510	0.505	0.500	0.495	0.490	0.486	0.481
-23	0.580	0.574	0.569	0.563	0.558	0.552	0.547	0.541	0.536	0.531
-22	0.640	0.633	0.627	0.621	0.615	0.609	0.603	0.597	0.592	0.586
-21	0.705	0.698	0.691	0.685	0.678	0.672	0.665	0.659	0.652	0.646
-20	0.776	0.769	0.761	0.754	0.747	0.740	0.733	0.726	0.719	0.712
-19	0.854	0.846	0.838	0.830	0.822	0.814	0.806	0.799	0.791	0.783
-18	0.939	0.930	0.921	0.912	0.904	0.895	0.887	0.879	0.870	0.862
-17	1.031	1.021	1.012	1.002	0.994	0.984	0.975	0.966	0.956	0.947
-16	1.132	1.121	1.111	1.101	1.091	1.080	1.070	1.060	1.051	1.041
-15	1.241	1.230	1.219	1.208	1.196	1.186	1.175	1.164	1.153	1.142
-14	1.361	1.348	1.336	1.324	1.312	1.300	1.288	1.276	1.264	1.253
-13	1.490	1.477	1.464	1.450	1.437	1.424	1.411	1.399	1.386	1.373
-12	1.632	1.617	1.602	1.588	1.574	1.559	1.546	1.532	1.518	1.504
-11	1.785	1.769	1.753	1.737	1.722	1.707	1.691	1.676	1.661	1.646
-10	1.950	1.934	1.916	1.899	1.883	1.866	1.849	1.833	1.817	1.800
-9	2.131	2.112	2.093	2.075	2.057	2.039	2.021	2.003	1.985	1.968
-8	2.326	2.306	2.286	2.266	2.246	2.226	2.207	2.187	2.168	2.149
-7	2.537	2.516	2.495	2.472	2.450	2.429	2.408	2.387	2.367	2.346
-6	2.765	2.742	2.718	2.695	2.672	2.649	2.626	2.603	2.581	2.559
-5	3.013	2.987	2.962	2.937	2.912	2.887	2.862	2.838	2.813	2.790
-4	3.280	3.252	3.225	3.198	3.171	3.144	3.117	3.091	3.065	3.039
-3	3.568	3.539	3.509	3.480	3.451	3.422	3.393	3.364	3.336	3.308
-2	3.880	3.848	3.816	3.785	3.753	3.722	3.691	3.660	3.630	3.599
-1	4.217	4.182	4.147	4.113	4.079	4.045	4.012	3.979	3.946	3.913
0	4.579	4.542	4.504	4.467	4.431	4.395	4.359	4.323	4.287	4.252

TABLE 2.—The vapor pressure of liquid water from  $-16^{\circ}$  C. to  $0^{\circ}$  C. (in mm. Hg)

Computed from Table 1 with the aid of the thermodynamic equation

$$\log_{10} \frac{p_v}{p_i} = \frac{-1.1489 t}{273.1 + t} - 1.330 \times 10^{-4} t + 9.084 \times 10^{-6} t^2$$

t	0.0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
$^{\circ} \text{C.}$										
-15	1.436	1.425	1.414	1.402	1.390	1.379	1.368	1.356	1.345	1.334
-14	1.560	1.547	1.534	1.522	1.511	1.497	1.485	1.472	1.460	1.449
-13	1.691	1.678	1.665	1.651	1.637	1.624	1.611	1.599	1.585	1.572
-12	1.834	1.819	1.804	1.790	1.776	1.761	1.748	1.734	1.720	1.705
-11	1.987	1.971	1.955	1.939	1.924	1.909	1.893	1.878	1.863	1.848
-10	2.149	2.134	2.116	2.099	2.084	2.067	2.050	2.034	2.018	2.001
-9	2.326	2.307	2.289	2.271	2.254	2.236	2.219	2.201	2.184	2.167
-8	2.514	2.495	2.475	2.456	2.437	2.418	2.399	2.380	2.362	2.343
-7	2.715	2.695	2.674	2.654	2.633	2.613	2.593	2.572	2.553	2.533
-6	2.931	2.909	2.887	2.866	2.843	2.822	2.800	2.778	2.757	2.736
-5	3.163	3.139	3.115	3.092	3.069	3.046	3.022	3.000	2.976	2.955
-4	3.410	3.384	3.359	3.334	3.309	3.284	3.259	3.235	3.211	3.187
-3	3.673	3.647	3.620	3.593	3.567	3.540	3.514	3.487	3.461	3.436
-2	3.956	3.927	3.898	3.871	3.841	3.813	3.785	3.757	3.730	3.702
-1	4.258	4.227	4.196	4.165	4.135	4.105	4.075	4.045	4.016	3.986
0	4.579	4.546	4.513	4.480	4.448	4.416	4.385	4.353	4.320	4.289

#### TEMPERATURE LAG OF THE OCEANS

551.463

By W. J. HUMPHREYS

[Weather Bureau, Washington, D. C.]

From time to time we see the assertion that any appreciable change in the temperature of the ocean, such, for instance, as might result from a change in the solar constant, persists, in large measure, over a period of years. These assertions, however, are not backed up by sound theory, but based, if upon anything at all, upon a few observations, which, for the particular long-range forecast, or other objects in view, it is convenient to assume explained in the alleged manner.

It may be helpful, therefore, to compute, according to known physical laws and constants, how great we reasonably may expect such lags to be.

Owing to wave action and convection, temperature changes of the ocean are not confined to the surface, but penetrate in approximately full magnitude to an appreciable depth. For calculation it is here tentatively assumed that an exactly equal change extends down 20 meters, and that beyond this depth there is no change. It is believed that this assumption is of the proper order. Anyhow, the results will be correct to within an experimental factor.

As is well known, the earth maintains its average balance between heat gained and heat lost, by radiating, in amount, as would a black body of the same size at the absolute temperature  $260^{\circ}$ .<sup>1</sup> It is also known that, on the average, temperature changes are roughly the same at the surface and all the way up through the troposphere, or convective portion of the atmosphere. Hence, if the surface of the earth should be kept at a slightly different temperature than heretofore, its planetary black-body temperature would also be altered in the same sense and to about the same extent.

The surface temperature of the land has a shorter time lag than that of the ocean, owing to permanency of position, lack of convection, and the small, as compared with water, specific heat of soil and rock. Actually, therefore, the temperature lags of the earth as a whole are less than they would be if there were no land at all, but for islands and many coastal regions not greatly less. Hence, to obtain the upper limit solution of the problem this land effect will be omitted. Perhaps this effect can best be

<sup>1</sup> Abbot and Fowle, *Annals Astrophys. Obs. Smithsonian Inst.*, 2, p. 175.